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171.1(c)(H) ENVIRONMENTAL ASSESSMENT

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2 PETITIONER: Alcide Corporation

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4 DESCRIPTION OF THE PROPOSED ACTION

4.1 REQUESTED APPROVAL

Approval is requested for the use of the system comprised of acidified sodium chlorite (ASC) solutions for use as an anti-microbial agent to reduce pathogenic and spoilage microorganisms on seafood or freshwater fish when used at a use concentration of 40 to 1,200 ppm within the pH range of 2.3 to 2.9.

The petitioned additive was originally approved as a Secondary Direct Food Additive (FAP 4A4433) on April 23, 1996 when new regulation 21CFR §173.325 was codified to reflect the acceptance of ASC for use as an anti-microbial agent in the processing of poultry meat as a component of a carcass spray or dip solution prior to immersion in pre-chiller or chiller waters, or for direct application in pre-chiller or chiller water solutions. Further approvals for the additive have been granted in the intervening period.

As of the date of submission of the current FAP, ASC is already approved for use on seafood or freshwater fish. This use was originally codified and/or listed on page 44122 of the Federal Register (Volume 64, No 156) on August 5, 1999 as follows:

§ 173.325 Acidified sodium chlorite solutions.

(d) The additive is used as an anti-microbial agent in water and ice that are used to rinse, wash, thaw, transport, or store seafood or freshwater fish in accordance with current industry standards of good manufacturing practice. The additive is produced by mixing an aqueous solution of sodium chlorite with any GRAS acid to achieve a pH in the range of 2.5 to 2.9 and diluting this solution with water to achieve an actual use concentration of 40 to 50 parts per million (ppm) sodium chlorite. Any seafood or freshwater fish that is intended to be consumed raw shall be subjected to a potable water rinse prior to consumption.

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- i) Alcide Corporation's present petition seeks to modify the current approval for the use of ASC solutions on seafood or freshwater fish to extend the dose and pH ranges as indicated earlier.

4.2 PROCESS DESCRIPTION

In ASC solutions, there are two components that are used to create the anti-microbial effect, the food-grade acid and the sodium chlorite. Both of these materials may initially be supplied at point of use as concentrates (typically for example 50% citric acid and 25% sodium chlorite), each of which is first separately diluted with water to form an intermediate liquid stream whose concentration is double the intended final use level. Alternatively, both materials may be formulated with stabilizers to create shelf-stable double strength solutions, which can then be shipped to the final use sites. In the final mixing step, sufficient acid is added to a 80 – 2,400 ppm solution of sodium chlorite to reduce its pH to the 2.3 - 2.9 range – typically pH 2.5 - and to create the desired final use concentration in the range 40 to 1,200 ppm. The resulting ASC solutions are then applied to the seafood or freshwater fish product surfaces by either spray or by immersion. In the case of a spray application, the liquid is dispensed from a spray apparatus in which either:

- ii) One stream each of the chlorite and the acid solutions are mixed at, or immediately before the spray nozzle, or;
- iii) A single stream of recently pre-mixed ASC solution is directed to the spray nozzle from a holding tank. The latter may be prepared prior to use, using ambient temperature or in cold temperature waters, so long as the chlorite and acid levels have been analytically determined to be within the acceptable range.

In the typical environment of a high-speed large volume seafood or freshwater fish processor, practical aspects of the process usually dictate that the product to be treated can only be exposed to the treatment solution for relatively short periods of time – usually measured in

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seconds. Thus where an ASC solution is applied by spray, this short exposure time will most likely dictate that the use concentrations will typically be at the upper end of the proposed use range i.e. between 500 to 1,200 ppm.

When an ASC solution is applied to seafood or freshwater fish by immersion in a high-speed processing environment, the actual period of immersion would typically also be relatively short thus the use concentrations would again tend to be in the upper use range. However in situations where seafood or freshwater fish is to be placed in iced storage or is to be contained for a period of time in a "wash tank" environment, then such immersion treatments could conceivably range anywhere from a few seconds up to several hours. In these situations, lower use concentrations and exposure times may be selected dependent upon the desired end point of the treatment process. Some of the factors, which may affect the choice of an immersion time and/or use concentration are listed as follows:

Rate of Kill

At the lowest use concentration of 40 ppm, the efficacy of an ASC solution, assuming constant maintenance of the treatment solution at the desired concentration, will be a direct function of the exposure time. Rate of kill as measured by Ct values will increase with the period of time over which the treated surfaces are exposed to the ASC solution. Thus for a 40 ppm use concentration, exposure times measured in hours may not be uncommon as being necessary to achieve significant impacts on the microbial populations that are present on seafood or freshwater fish. Conversely, at the highest use concentration of 1,200 ppm, extremely short exposure times – 30 to 120 seconds – may be all that is required to achieve the same significant impacts on microbial populations.

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Desired Efficacy Outcome

Where pathogen reduction is the desired outcome and the lowest use concentration is proposed, exposure times may need to be extended in 15 to 30 minute increments to achieve the necessary efficacy end point. Where spoilage organism control is the desired outcome, these exposure times may be measured in hourly increments. Conversely, at the highest use concentrations, significant pathogen reduction outcomes may be achieved in 15 to 30 second exposures and dramatic impacts on spoilage organisms – with subsequent extension of product shelf-life – may be seen with as little as 2 minute exposure times.

Seafood or freshwater fish Product to be Treated

Exposure times and use concentrations may also need to be modified dependent upon the seafood or freshwater fish product that is to be treated, simply to avoid any unnecessary or unacceptable impacts on the appearance or ultimate organoleptic qualities of the finished product.

4.3 NEED FOR THE ACTION

Millions of Americans become ill each year from something they eat. While diagnostic and surveillance methods for food-borne illness have improved dramatically in recent years, the exact number of cases can still only be approximated by government officials. As a result we must rely heavily on estimates when attempting to quantify the problem of food borne illness. As an example, the Centers for Disease Control and Prevention estimates that while deaths due to food poisoning have dropped from 9,000 to approximately 6,000 per year, the actual number of illnesses reported has risen to approximately 76 million per year. Much of this increase is attributed to better surveillance, more sensitive diagnostic techniques and more accurate diagnosis.

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Per capita, consumption of seafood or freshwater fish in the United States is rising.¹ As with other food processing systems where raw product is prepared for human consumption, seafood or freshwater fish – fish and shellfish – can be contaminated with both pathogenic and spoilage organisms during production (farming), harvesting, processing, distribution, handling and storage.

An estimated 11% of the food-borne outbreaks of illness in the United States are thought to involve seafood or freshwater fish, and 25% of these involve bacterial pathogens.² Such organisms include:

Salmonella spp.

Clostridium botulinum

Listeria monocytogenes

Vibrio cholerae

Vibrio parahaemolyticus

Vibrio vulnificus

One organism of particular importance in food borne illness is *Escherichia coli* O157:H7 which is reported to cause sickness in as many as 20,000 Americans each year through contaminated meats, seafood or freshwater fish and other sources. Of these infected people, up to 500 may die. This particular coliform organism, of animal fecal origin, is present in manure and animal droppings, which contaminate soil. Sewage sludge when allowed to flow into waterways or seaways untreated, contributes additional problems with respect to illness of seafood or freshwater fish origin. It is therefore easy to understand why it is that seafood or freshwater fish can readily enter the processing plant environment with significant levels of microbial contamination on their exterior surfaces, derived from organisms that were present in their environment during growth or from contamination that occurred during the harvesting or transporting processes.

Further, it is also evident that without careful attention to the implementation of

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appropriate practices to control these microbial contaminants during the preparation of the seafood or freshwater fish for processing, that these contaminants can easily be carried further along into the processing plant environment to ultimately contaminate the seafood or freshwater fish at the terminal handling stages.

Washing of seafood or freshwater fish with potable water after harvesting has most typically been the method used to render the product more acceptable from an overall appearance as well as possible contamination point of view. However, the primary purpose of washing is to remove excess or extraneous surface matter (e.g., soil, blood etc.) in order to gain an attractive appearance of the end product. While cleaning and washing processes do provide some limited reduction of the microbial load on most product surfaces, this method is not effective in rendering the final raw product sterile or even reducing the microbial load to a state of "disinfection."

Chlorinated water is often used in processing waters applied to seafood or freshwater fish during processing however its efficacy is readily dissipated by the presence of vegetable, soil and other organic matter. Thus at the typical use concentrations at which this material is applied the overall outcomes with respect to microbial reduction, tend to be relatively poor.

ASC was first approved by the US-Food and Drug Administration in 1999 for application to seafood or freshwater fish at a use concentration of 40 to 50 ppm and in a pH range of 2.5 to 2.9. At these use levels this anti-microbial intervention shows significant promise for the control of pathogen contamination and spoilage control. Despite this approval however, the need still exists to expand the use concentration and pH ranges of ASC in order to provide the seafood or freshwater fish industry with a more practical and more broadly useful anti-microbial intervention step that can safely be applied to all seafood or freshwater fish.

It is the position of Alcide Corporation that the proposed new ASC solution concentration and pH ranges which are the subject of this Food Additive Petition, and which have similarly already been approved by the US-FDA for use in poultry, red meat and produce processing (as

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well as for use, at the lowest concentrations, in seafood or freshwater fish processing), can play a major role in upgrading the overall microbial quality of seafood or freshwater fish in the United States.

4.4 LOCATIONS WHERE PRODUCTS WILL BE PRODUCED

There are two components to the ASC solutions being proposed for Secondary Direct Food Additive Status: the sodium chlorite or Base component, and the acidifier or Activator component needed to achieve the desired solution pH. The acidifier can be any one of a variety of US-FDA-approved GRAS acids, including but not limited to phosphoric, sulfuric, malic, acetic and citric. These are all materials of very high volume usage, and of many current and diverse applications in a wide variety of industries around the US today. These include:

- Liquid and powdered beverages
- Desserts
- Baked goods
- Meat pickling and fish preservation
- Jellies and preserves
- Candies
- Dairy products and cleaners
- Fats and oils (stabilizers)

The projected use volumes of any of these acids as an activator of sodium chlorite to generate an ASC solution are much below a fractional percentage of their other uses, thus the sites of production of these different acids, is not considered relevant to this environmental assessment.

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Sodium chlorite is currently being used as a chlorine dioxide (ClO_2) source in water treatment, as well as an industrial bleaching agent in a number of industries (primarily pulp and paper), in cleaning applications for the electronics industry, as a biocide in the food processing

industry, and in various applications in the oil industry. On April 23, 1996 the U.S. US-FDA first approved the use of sodium chlorite as a component of ASC solutions for microbial reduction pre-chill in poultry carcass sprays or dips and during the chill process as a component of the chill water. Thereafter, as a result of similar approval actions the US-FDA has also allowed for the use of ASC solutions for the following applications: i) pre- and post-chill in red meat carcass, carcass parts or organs sprays or dips; ii) pre-process on produce a.k.a. Raw Agricultural Commodities (RACs); iv) post-process on produce; and iv) in process waters on seafood or freshwater fish (the latter at use concentrations of 40 to 50 ppm and in the pH range 2.5 to 2.9).

The size of the worldwide sodium chlorite market is today estimated at 79.30×10^6 lb (36×10^6) Kg per year. Of this, the North American chlorite market is estimated to account for approximately 31% or 24.58×10^6 lbs (11.16×10^6 Kg) per year. European production of sodium chlorite accounts for an additional 42% of the worldwide production while Asia/Pacific production makes up the remaining 27%.^a Within North America, the largest producer of sodium chlorite is Vulcan Chemicals (Birmingham, Alabama) who produce approximately 23×10^6 lbs (10×10^6 Kg) per year at their facility in Wichita, Kansas. The balance of the North American production comes from Sterling Chemicals of Ontario, Canada. Major foreign production sites for sodium chlorite, which may be accessed if quality and economics are appropriate, include that of France's Atochem, S.A., Italy's Cafaro, and Spain's Energia Industrias Aragonesas in Madrid.

4.5 LOCATIONS WHERE THE PRODUCTS WILL BE USED

Once the pending FAP is accepted as a modification of the current regulation, the ASC anti-microbial solution will become available to all processors of seafood or freshwater fish as well as to a range of institutional facilities and home users. Geographically these solutions should find application in all areas of the country where seafood or freshwater fish are processed

^a Loic Le Dore. Welcoming address, Second European Symposium on Chlorine Dioxide and Disinfection. Paris, 24-25 June, 1999.

for final consumption. It is likely inevitable that there will be greater use of ASC solutions in those states which are recognized as being primary sources of seafood or freshwater fish including those where these products are harvested. For example, all of the coastal states, those states bordering the Great Lakes, the states of Mississippi and Louisiana - which are major suppliers of farmed catfish - and the state of Idaho which is a major supplier of farmed trout. Likewise, harvesting of crustaceans and farming of molluscs occurs around almost the entire coastline of the United States. Given the dominance of specific states in their respective seafood or freshwater fish production areas, relevant processing industries have naturally arisen to accommodate the further processing requirements of these various products. Overall therefore there is reason to believe that the potential for use of ASC solutions on seafood or freshwater fish covers the entire geographic area of the United States. But, it is this potential diversity of geographic and product use which also makes it extremely difficult to reach a reasonable estimate of the potential total annual usage for the ASC product.

IDENTIFICATION OF CHEMICAL SUBSTANCES THAT ARE THE SUBJECT OF THE PROPOSED ACTION

5.1 CHEMICAL NAMES AND PHYSICAL PROPERTIES

5.1.1 Sodium Chlorite (Appendix 1)

CAS Reg. No.:	7758-19-2
Color (31.25% Solution):	Colorless to light green
Specific Gravity:	1.21
Viscosity (@25°C):	1.62 cps
pH:	12.33

5.1.2 Acidifiers (GRAS)

Phosphoric Acid

CAS Reg. No.: 7664-38-2
Conforms with 21CFR §182.1073 as a Multiple Purpose GRAS Food
Substance

Citric Acid

CAS Reg. No.: 77-92-9 (anhydrous)
5949-29-1 (monohydrate)
Conforms with 21CFR §182.1033 as a Multiple Purpose GRAS Food Substance

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Hydrochloric Acid

CAS Reg. No.: 7647-01-0

Conforms with 21CFR §182.1057 as Multiple Purpose GRAS Food
Substance

Malic Acid

CAS Reg. No.: 617-48-1 DL mixture
97-67-6 L isomer

Conforms with 21CFR §184.1069 as a Specific Substance Affirmed as
GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as pH control agent
- (d) maximum use level

Sulfuric Acid

CAS Reg. No.: 7664-93-9

Conforms with 21CFR §184.1095 as a Specific Substance Affirmed as
GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as pH control agent
- (d) maximum use level

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Acetic Acid

CAS Reg. No.: 64-19-7

Conforms with 21CFR §184.1005 as a Specific Substance Affirmed as GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as a pH control agent
- (d) maximum use level

5.2 MODE OF ACTION OF THE GERMICIDAL SYSTEM

ASC chemistry is principally the chemistry of chlorous acid (HClO_2), a metastable oxy-chlorine species which decomposes to form chlorate ion, chlorine dioxide, and chloride ion.³ To better understand chlorous acid chemistry, a brief overview of the chemistry of various oxy-chlorine species follows.

As illustrated in Table I, chlorine can exhibit oxidation states from -1 to +7. As a consequence, its chemistry is varied and complex.

Table1. Oxidation States of Chlorine

ClO_4^-	+7	Perchlorate ion
ClO_3^-	+5	Chlorate ion
ClO_2	+4	Chlorine dioxide
ClO_2^-	+3	Chlorite ion
ClO^- or OCl^-	+1	Hypochlorite ion
Cl_2	0	Chlorine (molecular)
Cl^-	-1	Chloride ion

Oxy-chlorine species are important as oxidants in a number of applications. The strength of an oxidant is measured by its oxidation strength, or oxidation potential. Table 2 lists some of the more common oxidants, their associated oxidation reactions, their oxidation strengths

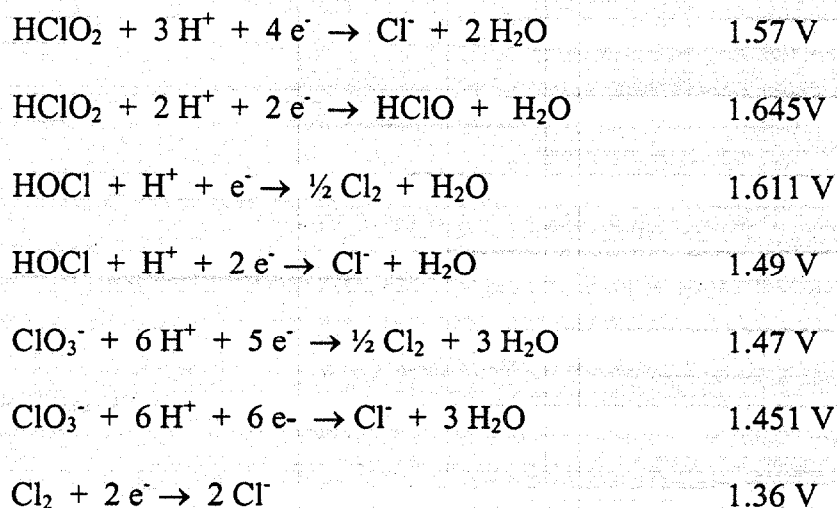
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(measured in volts), and their oxidation capacities (the number of electrons accepted by the oxidant). The chlorous acid (HClO₂) reaction, with its 1.57 V oxidation strength and 4-electron oxidation capacity, ranks just below ozone and the hydroxyl-radical generation reaction of hydrogen peroxide.

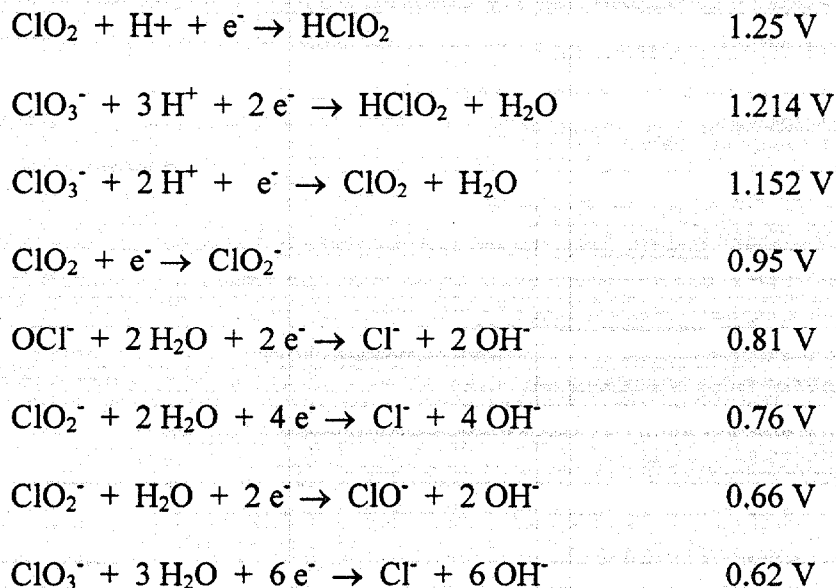
Table 2. Common Oxidation Reactions

Oxidant Reaction	Oxidant	Oxidation Capacity	Oxidation Strength (V)
$O_3 + H_2O + 2 e^- \rightarrow O_2 + OH^-$	Ozone	2e ⁻	2.07
$H_2O_2 + 2e^- \rightarrow 2 OH^-$	Hydrogen Peroxide	2e ⁻	1.78
$HClO_2 + 3 H^+ + 4 e^- \rightarrow Cl^- + 2 H_2O$	Chlorous Acid (Acidified Sodium Chlorite)	4e ⁻	1.57
$ClO_2 (v) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Vapor Phase)	1e ⁻	1.56
$HOCl + H^+ + 2 e^- \rightarrow Cl^- + H_2O$	Hypochlorous acid	2e ⁻	1.49
$HOBr + H^+ + 2 e^- \rightarrow Br^- + H_2O$	Hypobromous acid	2e ⁻	1.33
$ClO_2 + 4 H^+ + 5 e^- \rightarrow Cl^- + 2 H_2O$	Acidified Chlorine Dioxide	5e ⁻	1.51
$ClO_2 (aq) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Aqueous Phase)	1e ⁻	0.95
$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4 OH^-$	Chlorite	4e ⁻	0.78

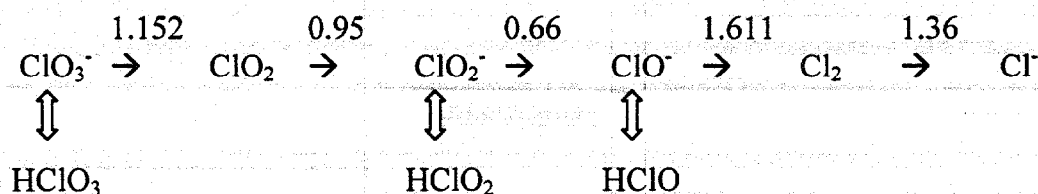
As mentioned before, oxy-chlorine chemistry is varied and complex. Listed below are oxidation half-cell reactions and their corresponding oxidation potentials for several additional reactions of oxy-chlorine species given by Gordon *et al.*,⁴ in the AWWA publication, *Disinfectant Residual Measurement Methods*:



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The oxidation potential diagram given below shows that chlorous acid is unstable with respect to disproportionation, i.e. chlorous acid is a metastable species.



Numerous researchers have determined that the decomposition reaction of chlorous acid is approximately second order with respect to chlorous acid.^{5, 6, 7, 8} At pH values above 2.0 where $[\text{ClO}_2^-] > [\text{HClO}_2]$, the rate law can be written as follows:

$$\frac{-d[\text{HClO}_2]}{dt} = k [\text{HClO}_2]^2$$

$$(\text{where } k = 0.023 \text{ M}^{-1} \text{ sec}^{-1} \text{ at } 25^\circ\text{C})^9$$

It is known that chloride ion accelerates the decomposition of chlorous acid and also alters the stoichiometry. Hong^{10, 11} developed the following empirical rate expression for the decomposition of chlorous acid, with the effect of chloride taken into account;

$$\frac{d[\text{ClO}_2]}{dt} = (m + nx) \left(1 - \frac{x}{\dots} \right)$$

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$$\frac{dt}{dt}$$

$$p + qx$$

$$\text{where } m = 2\{k_1[\text{HClO}_2]^2 + k_2[\text{ClO}_2^-][\text{HClO}_2]\}$$

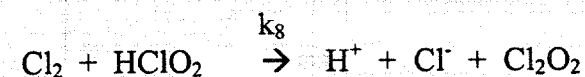
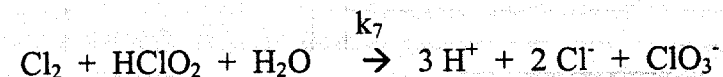
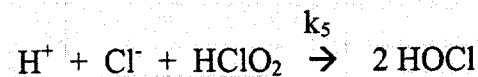
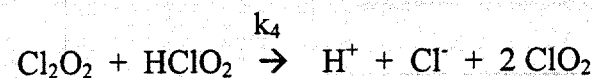
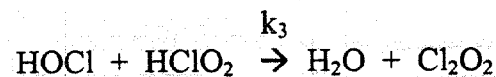
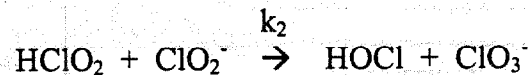
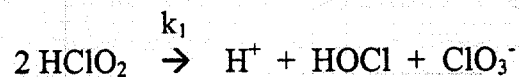
$$n = 4k_5[\text{H}^+][\text{HClO}_2]$$

$$p = \frac{k_3(k_7 + k_8)[\text{HClO}_2]}{k_6k_7[\text{H}^+]}$$

$$q = \frac{k_7 + k_8}{k_7}$$

$$x = [\text{Cl}^-]$$

Where the various rate constants refer to the following set of reactions:



In the absence of chloride, only the first four reactions need be considered. Doing this, Hong gives the following reaction equation, valid over the pH range of 0 to 3, for the initial rate

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law for the formation of chlorine dioxide:

$$\frac{d[\text{ClO}_2]}{dt} = k [\text{HClO}_2]^2 + k [\text{HClO}_2][\text{ClO}_2^-]$$

The rate of formation of chlorine dioxide given above, can be related approximately to the disappearance of chlorous acid by the following relation.⁸

$$-d[\text{HClO}_2]/4 = d[\text{ClO}_2]/2$$

In aqueous solution, chlorous acid, a relatively weak acid, dissociates as follows:

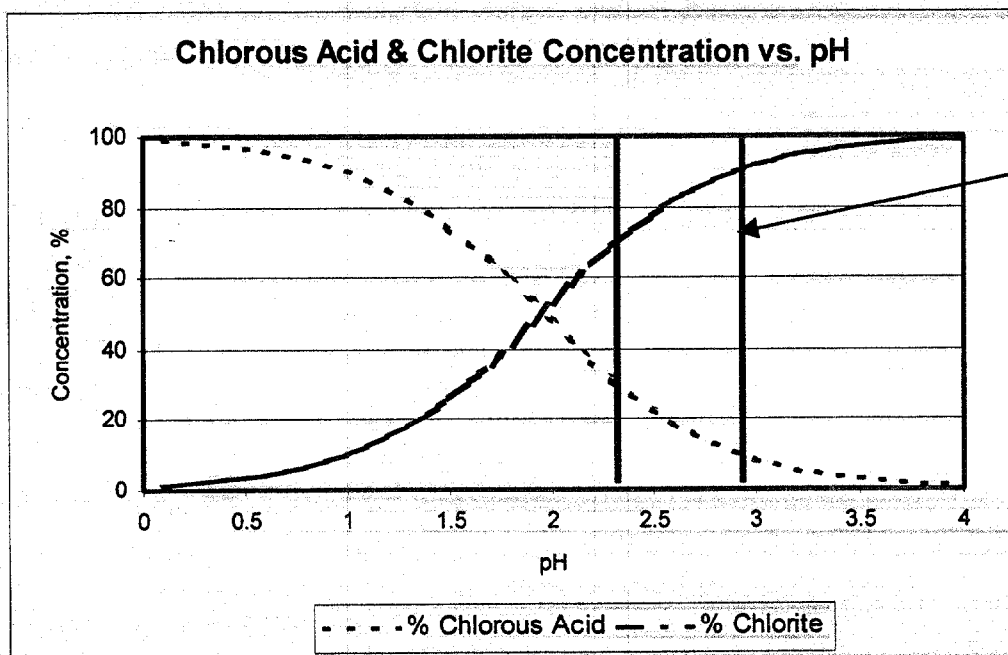


where K_a , the acid dissociation constant, is 1.01×10^{-2} at 23°C .¹² In terms of the acid dissociation constant (ionization constant) and the hydrogen ion concentration of the solution ($=10^{-\text{pH}}$), the chlorous acid concentration can be found from the total titratable chlorite concentration as follows:

$$\% \text{HClO}_2 = \frac{1}{1 + (1.1 \times 10^{-2})/[\text{H}^+]} \times 100\%$$

The following is a graph of this relationship.

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Typical ASC solution
operational range from pH
2.3 to 2.9

From this basic understanding of the chemistry and, combined with the results of microbiological testing, the optimal parameters for application of the ASC process as a short-term anti-microbial intervention on seafood or freshwater fish have therefore been determined to be

- i) A pH range of approximately 2.3 to 2.9;
- ii) A sodium chlorite concentration ranging from 40 ppm to 1200 ppm.

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INTRODUCTION OF SUBSTANCES INTO THE ENVIRONMENT

6.1 PRODUCTION RELEASES

As noted in Section 4, the ASC solution will be produced on site some time prior to application in the processing facility, be it a major operation, a contract operation for a specific chain, a supermarket facility, or ultimately even in the home. The solution mixing will take place through the confluence of the separate acid activator and sodium chlorite base solutions at some point prior to the final applicator nozzles. The acid and sodium chlorite solutions will typically be prepared in ambient temperature tap water although circumstances may arise where the solutions are prepared with chilled water down to temperatures as low as 4°C. Note that there may also even be circumstances where ASC solutions are frozen after initial constitution then ultimately allowed to, thaw gradually while in contact with the seafood or freshwater fish.

For freshly mixed solution application circumstances, the time that normally elapses between the creation/activation of the ASC solution and its final delivery to the surface to be treated is typically brief (no greater than 2 – 3 minutes). Thus, the levels of dissolved chlorine dioxide that might typically generate within the ASC solution over time will not exceed *ca.* 2 – 3 mg/liter (2 – 3 ppm).

In larger operations, it is anticipated that a spray treatment will be the primary mode of application to products which are the subject of this petition, in essentially the same manner as is currently commercially utilized for the pre-chill ASC treatment of various meat products and produce; i.e., the seafood or freshwater fish will pass through a semi-enclosed and baffled spray enclosure. The spray will be applied via pressurized spray nozzles, for varying exposure times up to about 30 seconds before the product exits the enclosure. In order to minimize the potential for possible off-gassing into the immediate worker environment, the semi-enclosed spray enclosure will be negatively pressurized via an aspirating air hose venting to the outside of the building. This will

ensure the removal of excess gaseous materials, while a dedicated drainpipe will route excess fluids to an enclosed drain for removal with other plant wastes. Short-term exposure, "immersion dip" processes may also be developed for some of the products that are the subject of this petition to conform with current industry practices vis-à-vis the inclusion of an anti-microbial into processing waters to reduce the spoilage-related microbial load of seafood or freshwater fish. As for the spray treatments, such systems would also be semi-enclosed and negatively pressurized via an aspirating air hose venting to the outside of the building to accommodate any potential worker safety issues.

In smaller operations where the application of product is expected to typically be limited to infrequent and/or small batch application using either hand-held "on/off-type" applicators or purpose-designed "dual-cylinder" hand-held spray bottles, the volume of product use and therefore the potential for off-gassing and worker environment exposure is significantly reduced compared to the larger commercial systems. As a result, no special precautions other than the inclusion of label precautionary statements regarding handling, adequate venting of the work area and use of the material are therefore anticipated.

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6.1.a. THEORETICAL WORSE CASE PRODUCTION RELEASES

While chlorine dioxide has a minimum tendency to form in ASC solutions when the chlorite and acid are initially combined immediately prior to spraying (typically measured as $< 2 - 3$ mg/liter dissolved in solution), it may exhibit an increasing tendency to form as the applied solution concentrates during the evaporative process or as a mixed but unused solution is allowed to "age." Thus, in a typical situation, the potential for chlorine dioxide entry into the air of the workplace would be expected to derive primarily from this evaporative source, more so than from that which is retained in solution. Chlorine dioxide also has a significant tendency to react with, and be degraded by soluble organic matter (such as soil) to form chlorite, chlorate and ultimately chloride. It is therefore expected that a major portion of both the initially projected chlorine dioxide maximum of $2 - 3$ mg/liter in solution and any quantity formed upon subsequent solution evaporation will be reduced to a non-volatile, chlorine-containing ion that will ultimately be removed in the organic matter laden waste waters of the processing plant.

Finally, it is further expected that the degree of chlorine dioxide evolution out of the ASC solution within the application enclosure during the treatment's maximum 30-second residence time on the seafood or freshwater fish will be low. This is particularly true because the high humidity conditions prevailing in the application cabinet will tend to suppress evaporation and therefore out-gassing of chlorine dioxide from the ASC solution. Thus the $2 - 3$ mg/liter level of chlorine dioxide that can typically be measured in an ASC solution within $2 - 3$ minutes of activation of sodium chlorite can be assumed to correspond to the most likely "maximum" amount of this substance that will arise from both initial and evaporative sources.

To put this into perspective from present day experiences with the application of ASC solutions in commercial poultry processing plants, a typical ASC spray operation applies 111 mL/kg of solution (1.67 fl. ozs. per 1.0 lb; average carcass is 3 lb) inside of a 2.45 m^3 spray enclosure over the course of 15.9 seconds^b. Therefore, in a "worst case" scenario where all of the

^b For a standard 90 bird per minute evisceration line a typical SANOVA spray cabinet enclosure measures $3 \times (0.67 \text{ m} \times 1 \text{ m} \times 1.22 \text{ m})$. Therefore internal volume = 2.451 m^3 . Average carcass exposure time to ASC chemistry while transiting the spray cabinet = cabinet length (3.66 m)/Line Speed. Line Speed = No. birds per second x shackle

dissolved chlorine dioxide were to be released into the environment, 450 kg (1,000 lb) of meat treated (333 carcasses), corresponding to 50 L of ASC solution applied^c, would theoretically release 150 mg of chlorine dioxide in 3.70 minutes (at the 3 mg/L concentration). Assuming a static air environment inside the application enclosure, with no venting or circulation of the air in the vicinity of the treated poultry meat, the dispersal of up to 40.54 mg of chlorine dioxide into 2.45 m³ of air in one minute would immediately raise its concentration above the OSHA 8-hour TLV of 0.3 mg/m³ and therefore lead to unsafe conditions both within the enclosure and in the immediate external environs.

For typical applications of ASC solutions to seafood or freshwater fish, it has already been established that the application volumes necessary for the achievement of significant pathogen reduction or for significant impacts on shelf-life have been established – based on depletion studies – to be approximately 84% of those used on poultry carcasses i.e. 93 mL/kg (1.24 fl. oz./lb) of seafood or freshwater fish, therefore the “worst case” concentrations of chlorine dioxide in the theoretical case described above would also be approximately 84% or up to 34.05 mg of chlorine dioxide into 2.45 m³ of air.

6.1.b. ACTUAL PRODUCTION RELEASES

Drawing on the current experiences with the application of ASC solutions in commercial poultry processing plants, air quality testing in the immediate area around commercial spray enclosures installed into poultry plants in the US shows that chlorine dioxide is generally undetectable (Appendix 2). Additionally, air quality testing of the air exhaust from these same commercial systems shows extremely low levels of chlorine dioxide present. These data clearly support the fact that the majority of the chlorine dioxide material that is in solution, remains so, and is ultimately disposed of in the liquid waste stream.

In an immersion or dipping operation there is not expected to be any change, certainly no

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width = (90/60) x 0.15 m. Therefore transit time = 3.66/0.23 = 15.9 seconds

^c 450 kg meat = 333 carcasses. At 90 birds per minute line speed 333 carcasses = 3.72 minutes of kill time. 450 kg meat x 111 mL/kg x 1 L/1000 mL = 50 L.

increase to the potential for air dispersal of either the ASC solution or of any dissolved chlorine dioxide, when compared to that of a spray operation. In fact, due to the likely accumulation of organic matter over time within the dip solution, plus the known interaction (reduction) of chlorine dioxide with organic matter it is anticipated that actual levels of this material in immersion or dipping operations will be lower than are typically seen in spray systems. However, as with the commercial spray systems that are currently being utilized in US poultry processing facilities, the environs surrounding an immersion or dipping operation will be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting to the exterior of the building.

Based on the above estimates, it is Alcide Corporation's belief that chlorine dioxide is unlikely to be a production release of any significance as a result of the proposed use of ASC in seafood or freshwater fish processing facilities.

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6.2 USE RELEASES

6.2.1 ESTIMATES OF RAW MATERIAL VOLUME

6.2.1.a INTRODUCTION

As previously mentioned in Section 4.4 of the Environmental Assessment, there is reason to believe that the potential for use of ASC solutions on seafood or freshwater fish covers the entire geographic area of the United States. But, it is this potential diversity of geographic and specific-product use which makes it extremely difficult to reach a reasonable estimate of the potential total annual usage for the product.

6.2.1.b SODIUM CHLORITE ESTIMATES

While the overall scale of the seafood or freshwater fish industry in the United States alone is enormous, surveys of industry need and evaluations of projected interest that have been conducted so far, suggest that the majority of "use interest" for ASC solutions is likely to be seen and expressed primarily by the highly controlled, value-added aquaculture industry. Finfish industries such as those of the deep sea trawling operations etc. appear to be less likely to be interested in utilizing an anti-microbial in the storage, processing or handling of their products. Thus best case "guestimates" of market penetration and market share would suggest that a realistic value for market uptake would be in the order of 25% of the aquaculture industry. Within North America, this market produced a total of 382×10^6 Kg (842×10^6 lbs) of product in 2000. The following table shows the major production species and quantities for the year 2000.

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US Aquaculture Market Production by Key Species (2000) and the Estimated Market Uptake for Acidified Sodium Chlorite

	Seafood or freshwater fish Type	Production (million lbs)	25% Market Uptake
Finfish	Baitfish	16.4	NA
	Catfish	596.6	149.2
	Salmon	39.1	9.8
	Striped Bass	9.7	2.4
	Tilapia	17.8	4.5
	Trout	60.3	15.1
Shellfish	Clams	10.7	2.7
	Mussels	0.5	0.1
	Oysters	18.7	4.7
Crustacea	Shrimp	4.6	1.2
	Crawfish	42.9	10.7
Other spp.		24.7	6.2
	Totals	842.0	206.4

As mentioned in the previous section, the projected application rate of ASC solutions onto seafood or freshwater fish has been evaluated in depletion studies and calculated to be in the order of 0.09 mgs/cm² of treated surface (approximately 93 mL/kg, 1.24 Fl. Oz. Per lb). Using this rate of application, the estimated use rate for ASC on seafood or freshwater fish can be recalculated as shown in the following table.

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**The Potential Annual Consumption of Sodium Chlorite from use as a
Processing Aid on US Seafood or freshwater fish Derived from
Aquaculture**

	Seafood or freshwater fish Type	25% Market Uptake (million lbs)	Use Volume (million gallons)	Sodium Chlorite (million lbs)
Finfish	Baitfish	NA	NA	NA
	Catfish	149.2	11.563	0.1157
	Salmon	9.8	0.756	0.0076
	Striped Bass	2.4	0.186	0.0019
	Tilapia	4.5	0.349	0.0035
	Trout	15.1	1.170	0.0117
Shellfish	Clams	2.7	0.209	0.0021
	Mussels	0.1	0.008	0.0001
	Oysters	4.7	0.364	0.0036
Crustacea	Shrimp	1.2	0.093	0.0009
	Crawfish	10.7	0.829	0.0083
Other spp.		6.2	0.481	0.0048
	Totals	206.4	16.008	0.1602

The total estimated ASC use volume of 60.60×10^6 L (16.01×10^6 gallons) on aquaculture product equates to a total sodium chlorite use – at the highest application rate of 1200 ppm – of 0.35×10^6 Kg (0.16×10^6 lbs) or 1.4% of the annual production of sodium chlorite in the United States.

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6.2.2 WATER AND AIR RELEASES

6.2.2.a INTRODUCTION

The components of the ASC solutions are the GRAS acid, of high purity, and the sodium chlorite (of a technical grade), which has sodium chloride and sodium chlorate as impurities. Upon acidification the chlorite, through chlorous acid, can be expected to minimally transform to chlorine dioxide and to chlorate. At the level of use of these components, and the minimum standing time for the mixed ASC solution, the amount of chlorine dioxide that is dissolved in solution will not exceed *ca.* 2 – 3 mg/liter. Being a highly reactive compound, this chlorine dioxide will quickly be reduced (by reaction with organic matter and with microorganisms on the seafood or freshwater fish surfaces) to even smaller quantities of chlorite and chloride ions. An even lower amount of chlorate will also be formed in this process by a separate pathway involving dis-proportionation of the chlorine dioxide.

As shown from the poultry plant data in previous Section 6.1, the air releases of chlorine dioxide are *de minimis*. Of greater possible interest are the relatively higher levels of sodium chlorite, i.e. 1,200 ppm as a maximum, of which the chlorite ion represents 895 ppm that might be reasonably expected to be disposed of into a processing plant's waste stream. The following projection puts this quantity into relative perspective, with respect to estimates of the total water volume throughput in seafood or freshwater fish processing plants.

Although no specific published data can be found on the quantities of water utilized in the diversity of water-washing operations where seafood or freshwater fish are processed, a projected level of chlorite release into processing plant effluent water can be derived from specific information made available from a current processor of farm raised salmon. In this processing plant, a single day's run of 77,180 Kg (170,000 lb) of salmon required 454,200 L (120,000 gallons) of water and/or ice for processing, in addition to other plant requirements for water such as transport of removed solids and overall plant sanitation. Calculations are confined, for the moment, to processing waters alone, and make use of the ASC application-rate estimate of 93

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mL/Kg (1.24 Fl. Oz/lb) of product treated. On that basis, 77,180 Kg of salmon would consume^d 7,177 L (1,896 gal) of ASC solution. This amount of solution would be diluted by the 454,200 L of daily processing water thereby effecting an approximate 63-fold reduction, in the concentration of chlorite in the waste stream. At a maximum use level of 1,200 ppm (1,200 mg/L, 1.25 oz/gal,) of sodium chlorite, the worse-case total amount of this material used per day would be approximately 8.61 Kg^e (18.96 lb), of which 6.42 Kg (14.14 lb) is the chlorite ion. Depletion studies have shown that approximately 10% of the chlorite ion is degraded as a result of the treatment or from reduction through contact with organic matter thus again the worse-case remaining mount of chlorite ion that might ultimately be available for dilution into the 454,200 L of processing water would be approximately 5.78 Kg (12.73 lb), reducing the final chlorite concentration to a theoretical final level of 13 ppm.^f

Since the plant waste-waters from all of the sanitary and house-keeping operations will contain additional organic matter, a major fraction of the available chlorite ion not already consumed, will further degrade on contact with this organic material. Additional factors which would be expected to result in a low to negligible chlorite ion load in the waste-waters of the plant include:

- i) The known instability of chlorite in the ASC system and its ultimate reduction predominantly to chloride.
- ii) The high reactivity of the oxychlorine species (chlorite, chlorate, chlorine dioxide) with soil and organic matter in general. (Refer to Section 7:0 – Fate of Emitted Substances in the Environment).
- iii) The zero chlorite ion profiles that naturally exist in the waste-waters of processing facilities utilizing an ASC system. (Refer to Section 7:0 – Fate of Emitted Substances in the Environment).

The fraction of chlorite that might therefore be expected to survive or remain in the

^d $(77,180 \text{ Kg} \times 93 \text{ ml/Kg})/1000 = 7,177 \text{ L}$

^e $7,177 \text{ L} \times 1200 \text{ mg/L} = 8.61 \text{ Kg}$

^f $5.78 \text{ Kg}/454,200 \text{ L} = 12.73 \text{ mg/L} = 13 \text{ ppm}$

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processing plant waste stream to ultimately be transported into an external treatment process such as a POTW is highly likely to be less than the LOD for chlorite i.e. <0.1 ppm.

For chlorate ion, the relative amount present in the waste stream, of a seafood or freshwater fish processing plant, assuming the above worse case scenario would be considerably less than the value calculated for chlorite. While this number can probably be estimated as a fraction of the chlorite that has been calculated, both compounds are expected to be present in such low amounts as to have a *de minimus* effect on local POTWs. For the purposes of this discussion therefore, chlorate levels will also be considered to be present at concentrations < 0.1 ppm.

The levels of acid used to achieve the requisite initial pHs of 2.3 to 2.9 for the ASC solutions are as follows (for a few representative GRAS acids):

Sulfuric acid, $<0.04\%$ (<400 ppm)

Phosphoric acid, 0.02 to 0.04% (200 to 400 ppm)

Malic acid, 0.04 to 0.08% (400 to 800 ppm)

Acetic acid, 0.50 to 1.0% ($5,000$ to $10,000$ ppm)

Citric acid, 0.50 to 1.2% ($5,000$ to $12,000$ ppm)

These levels are reduced by their subsequent dilution in the same quantities of water used for seafood or freshwater fish washing, transport and plant sanitation and are therefore of little environmental concern.

With respect to institutional or home use of ASC solutions vis-à-vis water discharges, the much greater ratio of organic matter to the small quantity of oxy-chlorine species in the ASC should result in virtually full degradation of these materials upon contact with the facilities' or home's waste systems.

In summary, worse case estimates of the oxy-chlorine species that might be expected to be

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present in the waste streams of processing plants that utilize ASC as an anti-microbial intervention on seafood or freshwater fish are:

Chlorine dioxide	<i>de minimis</i>
Chlorite	<0.1 ppm
Chlorate	<0.1 ppm

6.2.2.b IMPACT OF WATER RELEASES

Alcide Corporation does not believe that the above-indicated concentrations of oxychlorine species or food acids will have a negative impact on the operation of POTWs, for the following reasons:

- 1) Neither chlorite, chlorate nor chlorine dioxide is listed as an Interfering Substance in POTWs, as provided in Page 125 of the Wetzel document¹¹. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Chloride was listed as a potentially interfering substance, but at a level significantly higher (180 ppm) than its presence either as an impurity in the technical grade chlorite or if all the oxychlorines were converted to chloride. Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.
- 2) None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized anti-microbial, will have no effect at the *de minimis* levels estimated; neither can the chlorite, a much weaker source of activity, at the <0.1 ppm level estimated.
- 3) "(M)ost interference problems at POTWs are related to intermittent discharges of high-strength conventional wastes which overload a POTW's

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organic capacity, causing plant upset," according to an EPA reporter¹². The organic contribution of these systems is minimal, and the other common causes of plant interference are not a factor here:

- low pH[corrosion]
- solids or viscous pollutants.....[flow obstruction]
- high volatiles[explosion or fire hazard]
- heated discharges[altered biological activity]
- toxic discharges [inhibited biological activity]

6.2.2.c WATER RELEASES – SMALLER FACILITIES

It is anticipated that some ASC usage in the processing of seafood or freshwater fish will be distributed over a wide range of local facilities of low volume production, thereby reducing the "per site" ASC volume.

Because of the diversity of such small-use operations the prediction of specific ASC quantities with respect to other waters in the effluent of a particular type of facility is not feasible. However it can be readily concluded that the much smaller chlorite and acid quantities in the facility's effluent would be at least as likely to react with and be degraded by the organic matter in its effluent water as in the larger facilities. Once again, the maximum level of oxychlorines (mostly chlorite) that might be expected in the plant effluent of a seafood or freshwater fish processing operation is not expected to be greater than 0.1 ppm. The same basic calculations with respect to impact on POTWs apply.

6.2.2.d AIR RELEASES – LARGER AND SMALLER FACILITIES

As seen earlier, based on the commercial plant data that is available from ASC application in the poultry industry, the spray application of an ASC solution to seafood or freshwater fish is expected to create negligible air levels of chlorine dioxide, in an environment

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of normal air turnover, assuming the use of an appropriately designed spray cabinet enclosure to confine its dispersal and to control the gaseous and liquid effluents.

In ASC immersion dip operations, where seafood or freshwater fish will generally have some soil or other organic material on their surfaces this organic matter is also expected to destroy any small levels of chlorine dioxide that may have formed in the solution upon its activation. However, as with the SANOVA commercial spray systems currently used in commercial poultry and beef slaughter facilities, the environs surrounding an immersion or dipping operation in a seafood or freshwater fish processing plant will also be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting to the exterior of the building.

6.2.3. RELATION OF PLANT WATER RELEASES TO TOTAL PUBLICLY OWNED TREATMENT WORKS QUANTITIES

The industrial discharges to local Publicly Owned Treatment Works (POTWs), such as might be expected to occur from seafood or freshwater fish processing facilities, are further diluted by discharges from other industrial and non-industrial sources. The previous section of this petition discussed the relationship of such plant discharges to total POTW intakes. Reference was made to an EPA-sponsored study,¹⁵ that provided guidance in minimizing the discharge effects on these POTWs. In this report it was shown that the average influent wastewater from industrial sources was 26.3% of the total intake. That information was used to estimate the projected impact of the seafood or freshwater fish processing facilities using ASC treatments.

Using Alcide Corporation's estimates of market share, the application of ASC on processed seafood or freshwater fish would result in an overall increase in the POTW discharges attributable to sodium chlorite. However, as calculated in Section 6.2.2.a, the contribution from such a processor to its handling POTW is probably no more than the "worse case" estimates of <0.1 ppm.

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A similar analogy holds for the food-grade acids used for ASC activation, where the acid contribution to POTW facilities would be *de minimis*.

On the basis of these discussions, Alcide corporation does not believe that the above-indicated concentrations of oxy-chlorine species or food acids will have a negative impact on the operation of POTWs, for the following reasons:

- a) The levels of oxy-chlorines, *i.e.*, chlorite, chlorate, and chlorine dioxide, that would reach the POTWs, is at the parts per billion level, at most. Neither chlorite, chlorate, nor chlorine dioxide is listed as an Interfering Substance in POTWs, as provided in a document listing Interferences at POTWs¹⁵. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.
- b) None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized anti-microbial, will have no effect at the calculated parts per billion level; neither will the chlorite, a much weaker source of activity, at the minuscule levels possibly present.

6.2.4 COMPLIANCE WITH EMISSION REQUIREMENTS

Alcide Corporation fully anticipates that any seafood or freshwater fish processing operation that intends to use the ASC solutions, if deemed appropriate, will obtain the necessary permits and approvals for discharging process waters containing chlorite, chlorate and chlorine dioxide to POTWs. It should be noted that sodium chlorite, used in preparation of these ASC solutions, is an EPA-registered product. It is Alcide Corporation's current intention to use one of three EPA registered sodium chlorite products for the proposed application (or the equivalent):

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Vulcan Chemicals 79% Technical Sodium Chlorite, Technical Sodium Chlorite Solution 31.25, or 31% Active Sodium Chlorite Solution. Copies of the Technical Data Sheets and Material Safety Data Sheets for these products are provided in Appendix 2 of this section. Alcide Corporation intends to request that Vulcan Chemicals include label copy, which mandates that users of the sodium chlorite must discharge the solutions in accordance with the requirements of the facility's National Pollution Discharge Elimination System permit. Any warning statements on the labels concerning the hazard of the products to organisms that may be exposed to it in the environment will also be on the labels of the FDA-regulated use.

6.2.5. COMPLIANCE STATUS

Sodium chlorite has a number of commercial uses, primarily as a source of chlorine dioxide, *e.g.*, pulp and paper bleaching, drinking water treatment, as a slimicide in cooling towers, as a food disinfectant, and as a cleaning agent in the electronics industry. The current U.S. production of sodium chlorite is close to 11.16×10^6 Kg.

As shown in Section 6.2.1 of this petition, in the estimates of "worse case" usage that Alcide Corporation has made, the total maximum projected use of sodium chlorite for seafood or freshwater fish, was estimated at 0.35×10^6 Kg (0.16×10^6 lbs) or 1.4% of the total sodium chlorite market in the US. Accordingly Alcide does not believe that approval for the proposed use will affect current compliance by sodium chlorite producers with environmental regulations.

Use of the food grade acid activators is significantly less, of a larger total commercial utilization, and a similar conclusion is drawn for these materials as well.

7 FATE OF EMITTED SUBSTANCES IN THE ENVIRONMENT

7.1. Introduction

Chlorine dioxide (produced from sodium chlorite) is used widely in drinking water treatment in the U.S. When chlorine dioxide reacts in drinking water, approximately 50 - 70% is converted back into chlorite and the remainder into chloride and chlorate. The MCL (Maximum Contaminant Level) for chlorite in drinking water is 1.0 ppm, corresponding to 1.34 ppm sodium chlorite. The Rfd (reference dose) for the chlorate ion is much higher than that for chlorite, and therefore the US EPA (Environmental Protection Agency) has not set a MCL for the chlorate ion. Under The Emergency Planning and Community Right-to-Know Act statute (40 CFR Sect. 313 TRI), the US EPA considers chlorine dioxide releases to the environment at levels below 1.0 ppm to be *de minimis*. Because chlorine dioxide decays rapidly into chlorite, chloride and chlorate, this limit is reflective of the low environmental toxicity of those ions as well.

The chlorite ion is thermodynamically unstable with respect to other chlorine species, e.g., hypochlorite and chloride. It reacts rapidly with Fe(II) and Mn(II) as well as with reduced sulfur species and organic compounds. It is also rapidly degraded photochemically. Consequently, it does not persist in the environment.

In the following, some of the aqueous reactions of the chlorite ion are examined along with its photochemical degradation.

7.2. Chemical Degradation of Chlorite

In acid media, the chlorite ion is in equilibrium with chlorous acid



Below a pH of ~3.5 the following mechanisms predominate



The positive oxidation potentials indicate that the reactions proceed spontaneously as written. The hypochlorous acid, HClO, produced from the second reaction rapidly reacts to produce chloride ion as shown in the following pathway:

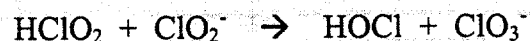


This reaction is much faster than that of hypochlorous acid with organics. Consequently, very few chlorinated organics are formed.

At higher pH values, chlorite can degrade by one or both of the following pathways:



Chlorite can also undergo disproportionation reactions (reactions in which two or more molecules of one species react to seafood or freshwater fish one species with a higher oxidation state along with one of lower oxidation state). This is illustrated in the following reaction in which chlorite/chlorous acid (oxidation state +3) decays into hypochlorous acid (oxidation state +1) and chlorate (oxidation state +5):

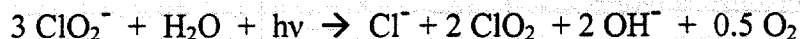


Fabian ¹⁷ demonstrated that iron(III) catalyzes the decomposition of chlorite. Iatrou *et al.* ¹⁸ investigated the feasibility of using ferrous iron (Fe(II)) to reduce chlorite concentrations.

Laboratory tests indicated a required reaction stoichiometry of 3.0 - 3.1 mg Fe(II)/mg ClO₂⁻. The reaction rate was rapid for pH values of 5 and greater. Interference from dissolved oxygen was minimal. The ferric hydroxide solids produced as a by-product for the Fe(II)-ClO₂⁻ reaction had no adverse effect on alum coagulation for the removal of turbidity and dissolved organic carbon. Iron catalysis of chlorite is an important degradation pathway in both soils and wastewater streams.

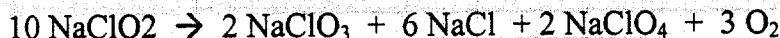
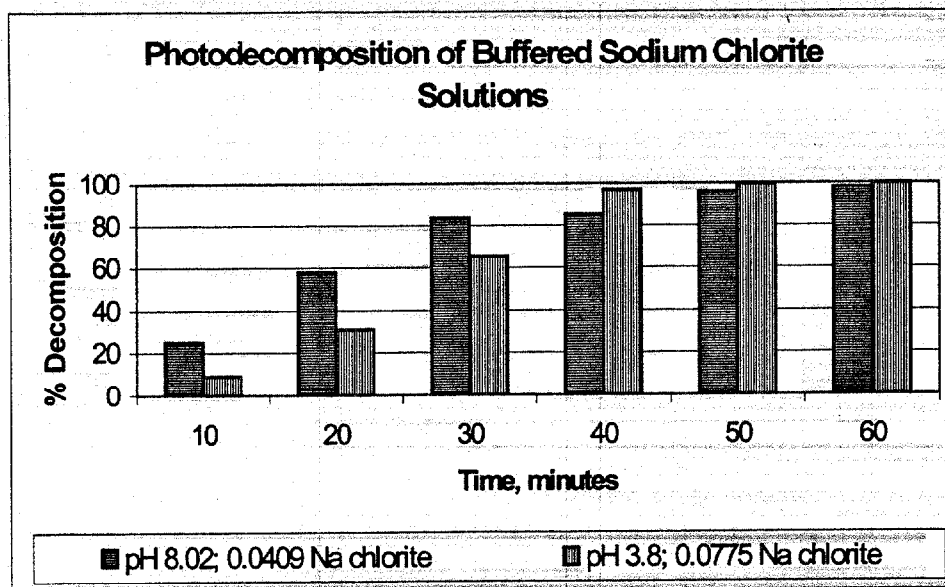
7.3. Photochemical Degradation of the Chlorite Ion

Buxton and Subhani ¹⁹ indicated that the chlorite ion undergoes photolytic decomposition to form chlorate, hypochlorite, chlorine dioxide and oxygen. The results of work by Cosson *et al.* ¹⁹ suggest that chlorate is not formed by direct photodecomposition of chlorite, but rather by decomposition of chlorine dioxide. Their results are consistent with the stoichiometry



Unless the chlorine dioxide formed from the photolysis of sodium chlorite solutions is removed from solution as soon as it is formed (e.g., via an air sparge) it is rapidly degraded into chlorate and chloride.

In 1964, Nabar *et al.* ²⁰ published the results of their work on the photodecomposition of chlorite. The following figure shows their results for the fadeometer decomposition of a 0.0409 N NaClO₂ solution (3699 ppm) buffered at pH 8.2 and a 0.0775 N NaClO₂ solution (7009 ppm) buffered at pH 3.8. The half-life of the higher pH solution was less than 20 minutes; that of the pH 3.8 solution was less than 30 minutes. Decomposition of chlorite solutions by sunlight was reported to be significantly faster. Nabar *et al.* suggested the following photochemical reaction pathways for the degradation of chlorite under alkaline and acidic conditions, respectively:



In other work, Zika *et al.*²¹ found that chlorite has a half-life of less than 10 minutes in direct sunlight. More recently, Wang²² determined that chlorite solutions degraded rapidly (half-life ~ hours) under laboratory fluorescent lighting and even more rapidly in direct sunlight (half-life ~ minutes). This was verified in a field trial at the Los Angeles Country Reservoir²³ in which chlorine dioxide was applied to control algal blooms. Chlorine dioxide was applied at night to give adequate reaction time with the algae present. Within four hours after sunrise, levels of, both chlorine dioxide and its primary degradation byproduct, chlorite, were below detection limits.

7.4. Chlorite Degradation in Soil

In 1999, Certified Laboratories (Plainview, NY) conducted a study (Appendix 3) to simulate the rate of degradation of a spilled chlorite-containing product (Alcide 4XLA Teat Dip, 2400 ppm chlorite acidified with lactic acid to a pH of 3.0). Three different soil samples differing in moisture

and organic content were used. The results are shown in the following table. It was assumed that in a spill the product would be diluted 1:10. The last column gives the time at which the chlorite level was below the analytical detection limit (~20 ppm in the soils studied).

The rate of degradation was clearly a function of organic loading and also of soil moisture. From these samples, chlorite is not expected to be persistent in soils, and consequently will not have an adverse impact on the environment.

Chlorite Degradation in Soil				
Characteristics of Soil Samples				
Sample	Moisture, %	Organics Dry Basis	Organics Soil Basis	Chlorite to "0.0"
A	30.0	13.34	9.34	4 hours
C	3.2	0.72	0.9	8 days
E	44.2	53.07	29.6	8 hours

7.5. Chlorite Degradation in Manure

In another study (Appendix 4), ASC was added to cow manure at an initial level of 229 ppm. Aliquots were analyzed over a two-day period. The results, in the table below, show that the chlorite levels had declined approximately 91% (to the 20 ppm detection limit of the method) within 24 hours.

Chlorite Degradation in Manure	
Exposure time (hours)	[Sodium Chlorite] ppm
0	229
0.33	217
0.75	213
1.25	45
4.0	45
5.0	49
15	45
24	20
48	20

Note: Method detection limit was ~20 ppm.

7.6. Chlorite Degradation in Poultry Processing Waste Waters

A study was conducted to evaluate the persistence of sodium chlorite in typical poultry processing wastewaters (Appendix 5). Samples of wastewater containing spent ASC (ASC) treatment solution were collected from four poultry processing plants immediately prior to discharge to the local POTW (publicly owned treatment works), cooled, and shipped to a third-party laboratory for chlorite analysis. Samples were protected from UV exposure during the analytical process.

The following table gives specifics for the four plants where these samples were taken, as well as the calculated chlorite levels in the wastewater. The ASC solution as applied is 1,000 ppm sodium chlorite. Typically, 90% of the applied solution goes to drain. The sodium chlorite in this spent solution typically measures 900 ppm.

NaClO ₂ Concentrations in 4 Poultry Processing Facilities Using ASC					
Plant	Processing Rate Birds/Day	ASC Usage oz/bird	ASC Usage GPD	Total Plant Wastewater MGD	Calculated [†] [NaClO ₂] ppm
1	232,050	6 oz	10,877	1.5	5.9
2	156,500	6 oz	7,336	1.5	3.96
3	154,833	6 oz	7,258	1.3	7.64
4	170,260	6 oz	7,981	1.2	5.39

[†]Calculated chlorite in plant effluent = ASC Usage 90% (900 ppm/Total Plant Wastewater)

When the samples were analyzed (Ion Chromatography, EPA Method 300.1), both chlorite and chlorate were not detected, indicating that chlorite is not persistent in the environment.

Furthermore, before discharge into the environment these wastewaters are commingled with other industrial wastewater discharges and domestic wastewaters. Assuming a typical POTW processes 25 MGD, any chlorite from the plants is diluted by a factor of 15-20 (25/1.5 to 25/1.2) using the examples above. The resulting calculated concentration of chlorite contribution to the total effluent entering POTW waters would be well below the 1.0 ppm MCL for drinking water, albeit no degradation occurs.

7.7. Conclusion

Theory predicts, and lab studies and analyses of actual samples (soil, manure, wastewater) confirm, that chlorite decays rapidly in the environment and is not expected to exert any adverse impact.

8 ENVIRONMENTAL EFFECTS OF RELEASED SUBSTANCES

8.1 EFFECTS ON AQUATIC ORGANISMS

Summaries of the aquatic-toxicity of relevant oxy-chlorines that might enter the environment as a result of processed seafood or freshwater fish treatment are provided in the next paragraphs. Following the discussion of each specific oxychlorine is a projection of the effects from each of these materials as a result of the treatment of seafood or freshwater fish.

Sodium Chlorite: The LC₅₀ aquatic toxicity to fish and oyster species ranges from 41 to 149 ppm, and from 0.151 to 0.650 ppm for *Daphnia magna* and Mysid shrimp, resp. The US-EPA has determined that sodium chlorite is toxic to fish, on the basis of the *Daphnia magna* figure. It was shown in Section 6.2.2.b. that a theoretical worse case maximum level of about <0.1 ppm of sodium chlorite would reach the typical POTW.

During subsequent waste-water treatment or at the POTW, chlorite will mix with other organic laden waters and be rapidly reduced. For effluents that might not be directed to POTWs, but are directed to catch ponds and leaching beds, the high levels of organic matter in the earth environment would rapidly reduce the chlorite to safe levels before the entraining water reached habitable waters for aquatic species.

Sodium Chlorate: The LC₅₀ for freshwater and marine fish is consistently >1000 ppm.

Sodium chlorate, being a small fraction of the impurities in technical grade sodium chlorite, and forming to a *de minimis* extent during the degradation of ASC solutions, is therefore of no concern from their use in product treatments. This conclusion is also directly applicable to the lower volume use of ASCs for treatment of processed seafood or freshwater fish.

Chlorine Dioxide: The rapidity of degradation of chlorine dioxide in organic

environments, coupled with its *de minimis* production in ASC solutions eliminates any aquatic toxicity concerns from product treatments. This conclusion is also appropriate for effluents resulting from ASC use on processed seafood or freshwater fish.

8.2. EFFECTS ON TERRESTRIAL ORGANISMS

A broad variety of toxicological studies have been carried out on the oxychlorine species chlorite, chlorate and chlorine dioxide, in connection with the worldwide use of chlorine dioxide in the disinfection of potable water. The ClO_2 has been found to seafood or freshwater fish virtually no chlorinated hydrocarbons as potential mutagens, as does chlorine. On a concentrated basis, the oxychlorines have been found to cause oxidative changes to erythrocytes, both in loss of structural integrity and formation of methemoglobin. However at the parts per billion levels that it is expected that these materials will be found in seafood or freshwater fish processing plant effluents, the data obtained in connection with drinking water levels of the oxychlorines are more relevant.

On an acute basis, the toxicity of sodium chlorite is in the range of 300 - 350 mg/kg, based on the LD_{50} values for mice, rats, and guinea pigs. For sodium chlorate, the LD_{50} range from ~600 to 8000 mg/kg for mice, rats, dogs, cats and rabbits. With respect to the acute toxicity of chlorine dioxide, an LD_{LO} of 500 ppm was found for 15 minutes air exposure by rats. In man, a 5 ppm level in the air was found to be an irritant to the respiratory and gastrointestinal tracts. Such levels would not be found in seafood or freshwater fish processing plants.

A variety of sub-acute studies have been conducted on animals and human volunteers, who ingested waters containing up to 40 ppm of chlorine dioxide in a single episode, or 5 ppm solutions of chlorine dioxide or sodium chlorite for a 12 week period. In the latter case there were some effects on blood chemistry, but little other effects. In the former case there was headache, nausea and abdominal discomfort which passed in 5 minutes.

U.S. EPA's recently completed re-assessment of chlorite and chlorine dioxide safety has

established a Reference Dose (RfD) for both of these materials of 0.03/mg/kg/day in drinking water, based on an NOAEL (No Observable Adverse Effect Level) of 3 mg/kg/day and a 100-fold safety factor²⁴. This corresponds to 2.1 mg/kg/day intake of chlorite or chlorine dioxide for a 70 kg individual. The report of the American Water Works Association's evaluation of chlorite and chlorate residues established a NOEL for chlorate of 78 mg/kg/day, which, translates to a maximum intake of 54.6 mg of chlorate per day for a 70 kg person, including the 100-fold safety factor²⁵.

On the basis of the oxidative tendency of these oxychlorine species to be chemically reduced by organic matter in seafood or freshwater fish processing plant waters, and subsequent municipal water treatment facilities, the levels of the three oxychlorine species are anticipated to be significantly lower in waste waters than are the actual levels calculated to be of minimal risk to individuals.

8.3 ENVIRONMENTAL BENEFITS

The use of ASC acid systems for treatment of seafood or freshwater fish offers the possibility of several environmental benefits:

8.3.1 NON-FORMATION OF MUTAGENS AND CARCINOGENS

In those instances where ASC solutions might be used, or are used in place of chlorinated water for disinfecting seafood or freshwater fish surfaces, the potential for the formation of chlorinated organic materials in the environment would be significantly reduced.

8.3.2. REDUCTION IN AQUATIC TOXICITY

Similar considerations would apply to the reduction of hypochlorite in aquatic environments, which has the following toxicity:²⁶

- Cold water fish 0.132 – 135 ppm (LC₅₀-96 hr)
- Warm water fish 0.28 - 2.1 ppm (LC₅₀-96 hr)
- *Daphnia magna* 0.037 - 2.1 ppm (LC₅₀-48 hr)

These data indicate that chlorine/hypochlorite is much more toxic to both cold and warm freshwater fish than is chlorite or chlorate, and generally slightly more toxic to the *Daphnia magna* invertebrate.

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9 USE OF RESOURCES AND ENERGY

As estimated earlier in Section 6, in the worse case scenario, if the total seafood or freshwater fish uses of ASC were to follow the market penetration assumptions made, the amount of additional sodium chlorite consumed would be 1.4% of the total present consumption of sodium chlorite. Therefore, the impact on national resources and energy by such incremental use will be of minimal significance. Also no minerals will be used in the preparation or production of the subject additive. Environmental releases of chlorite, chlorate, chlorine dioxide and any of the GRAS acid activators are not expected to adversely affect threatened or endangered species nor impact historic structures.

10 MITIGATION MEASURES

No adverse environmental effects are anticipated from residual "worst-case" levels of chlorine dioxide as a result of use of the subject additive, if this petition is approved. Therefore, no mitigation measures are required.

11 ALTERNATIVES TO PROPOSED ACTION

Inasmuch as no potential adverse environmental effects are expected to occur, no mitigation alternative actions are necessary.

12 PREPARER

This Environmental Assessment was prepared by G. Kere Kemp, Chief Scientific Officer of Alcide Corporation. Dr. Kemp has an educational background in Veterinary Science. His 28 years of work experience have been primarily directed toward the fields of microbiology, pharmacology and pharmacotherapeutics with specific focus on the development and registration of novel and unique anti-microbial substances for potential uses in animal, human and industrial applications.

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13 CERTIFICATION

The undersigned official certifies that the information presented is true, accurate and complete to the best knowledge of the firm.

Date: November 15th, 2002

Signature:

Name:

G. Kere Kemp

Title:

Executive Vice President

Chief Scientific Officer

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14 APPENDICES

Appendix 1. Sodium Chlorite Technical Data Sheets and Materials Safety Data Sheets.

**Appendix 2. Carlisle Consulting, Inc. *Air Sampling Survey for Chlorine & Chlorine Dioxide:*
1999, Harrison, Arkansas**

**Appendix 3. Certified Laboratories, Inc. *Degradation of Chlorite in Soil – Final Report on
Performance of Protocol of 3/24/1999.* 1999, Plainview, NY.**

**Appendix 4. Certified Laboratories, Inc. *Degradation of Chlorite in Cow Manure.* 1999,
Plainview, NY.**

**Appendix 5. ABC Research Corporation. *Determination of Chlorite, Chloride and Chlorate in
Waste Stream Waters.* 2000, Gainesville, FL.**

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